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Concentration of organic compounds in natural waters with solid-phase dispersion based on advesicle modified silica prior to liquid chromatography

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Abstract

The ability of vesicle-coated silica to aid the extraction of organic compounds from water prior to liquid chromatographic analysis is presented for the first time. The method is based on the formation of silica supported cationic multi-lamellar vesicles of gemini surfactants inherently ensuring the presence of hydrophilic and hydrophobic sites for the partitioning of analytes bearing different properties. Method development is illustrated by studying the adsolubilization of UV absorbing chemicals from swimming pool water. Due to the requirement for external energy input (intense shearing) a method based on solid-phase dispersion (SPD) was applied producing better results than off-line solid-phase extraction (SPE). Meticulous investigation of the experimental parameters was conducted in order to elucidate the mechanisms behind the proposed extraction pattern. Analyte recoveries were quantitative under the optimum experimental conditions offering recoveries higher than 96% with RSD values below 5%.

Keywords: Advesicles; Solid-phase dispersion; Liquid chromatography; Water samples

1. Introduction

Over the past decade, surfactant-based analytical chemistry has rapidly evolved to become one of the most challenging parts of contemporary analytical science. A relatively new concept in the analytical applications of organized surfactant assemblies is their property to organize on various surfaces in a two-dimensional orientation thus giving rise to what is called ad- or hemi-solubilization [1]. This phenomenon refers to the micellar aggregation of ionic surfactant monomers on oppositively charged surfaces, mostly of metal oxides such as alumina, silica, titanium dioxide and ferric oxyhydroxides providing solubilization sites for the partitioning of organic substances. The phenomenon is controlled by the hydrophobicity of the adsolubilizates as well as the microenvironment of the surfactant adsorbed layers and is described by a four region adsorption process (when presented in a double logarithmic scale) which defines the type and shape of aggregates on the surface. It is therefore conceivable that the surpass of a critical concentration is required to allow surfactants to assemble on a given surface but the type of aggregate formed is still subject to controversy [2].

Compared to other micellar media adsolubilization offers several analytical advantages. In the first place, they provide more hydrophobic environments than conventional micellar media approximating the properties of 1-octanol or ethyl acetate [3]. At the same time, the co-adsorption of weak acids or bases, is two to three times larger than the corresponding micellar solubilization constants which enables the efficient partitioning of charged species [4]. Furthermore, the overall process is not only determined by surfactant/surfactant interactions under the solution conditions but also from surfactant/mineral interactions, which defines the aggregate structure on the solid surface. Thus, depending on the concentration either ad- or hemi-micelles can be formed providing different solvation properties for various organic solutes with different polarities [5]. All these advocate to the achievement of high preconcentration factors, competing solid-phase extraction (SPE) for the concentration of various analytes at the ultra low levels. The limitations of these methods lie in the dissociation of surfactants from admicelles that reduces the sample loading capacity and the low tolerance for inorganic electrolytes due to competition with the surfactant

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for the adsorptive sites of the alumina surface which limits their application to samples with low salt content (<0.2 M) [6,7].

On the other hand, although a wealth of studies are available on the adsorption of cationic surfactants on various surfaces, no previous study describing such a system for analytical purposes has been presented. Moreover, all analytical methods published hitherto are focused on the formation of micelle-like structures neglecting the potential of vesicles to adsorb on mineral oxides. Thus, the immobilization of ionic surfactant vesicular aggregates on mineral surfaces is an unexplored field of research. However, unlike micellar clusters where a critical concentration gradient should be reached, vesicles inherently ensure the partitioning of polar and apolar analytes due to their structure, consisting of one or more bilayers arranged in a hollow, closed geometry, which incorporates both hydrophilic and hydrophobic cores [7,8]. Nevertheless, a central point in the analytical application of vesicles has been their preparation since many surfactants with vesicle-forming properties are limited and commercially not available. Moreover, the preparation of vesicles by mixtures of anionic–cationic surfactants (catanionic vesicles) or the use of cosurfactants to aid the process are usually cumbersome and require strict adherence to the experimental procedure since minor deviations can cause dramatically different morphologically structures [9,10]. More serious still, all methods involving the use of vesicles published so far deal with their application in liquid–liquid extraction procedures and the only known applications of supported vesicles is their utilization as stationary phase modifiers in liquid chromatography and capillary electrophoreses [11,12].

Symmetric salts of quaternary ammonium surfactants are the most common double-chained ampliphiles of which didodecyldimethylammonium bromide (DDAB) is perhaps the most frequently investigated. Motivated by the fact that DDAB, spontaneously gives birth to vesicular structures in aquatic solutions [13], we investigated the ability of cationic vesicles to adsolubilize on the negatively charged silica surface and interact with organic species in solution. Personal care products residues (commonly deployed in sunscreen formulations) were extracted from swimming pool water under the optimum experimental conditions. The obtained extracts were analyzed by high performance liquid chromatography and UV detection revealing that the proposed methodology offers high recoveries and preconcentration factors. To our knowledge, this study is the first reporting on the analytical utility of supported vesicular aggregates as a new alternative for the concentration of organic amphiphiles from aqueous matrices.

2. Experimental

2.1. Reagents and materials

All reagents used were of analytical reagent-grade. DDAB was obtained from Aldrich. Working solutions of 5×10^{-2} M were prepared weekly in doubly distilled water. Eusolex 232 (2-phenylbenzimidazol-5-sulfonic acid sodium salt, $\log K_{ow} = 0.16$), Bz-3 (2-hydroxy-4-methoxybenzophenone, $\log K_{ow} = 3.52$), Eusolex 6300 (3-(4-methylbenzyldene)-camphor, $\log K_{ow} = 5.47$) and Eusolex 2292 (octyl methoxy cinnnamate, $\log K_{ow} = 5.80$) were purchased from Merck (Darmstadt, Germany). Stock standard solutions of 100 mg/L were prepared weekly in methanol (or water for E232) and stored in dark at 4 °C. Working solutions were prepared daily in doubly distilled water upon appropriate dilution. Working solutions of 60×10^{-3} M of 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (HEPES) buffer (pH 8.2) (Fluka) were prepared in doubly distilled water. Acetonitrile, methanol and water (HPLC-grade) were obtained by Labscan. Finely ground amorphous microcrystalline silica dioxide was supplied by Sigma. The physical properties of this mineral oxide were as follows: particle size distribution 0.5–10 μm with approximately 80% between 1 and 5 μm; mean 2.5 μm; surface area 220 m^2/g; density 0.144 g/cm^3. Sodium dodecyl sulfate (SDS (Sigma), Triton X-114 (Aldrich) and cetyltrimethylammonium bromide (CTAB, Fluka) were used without further purification. $NaNO_3$ (Fluka), KCl (Mallinckrodt), NaBr (Fluka) and NaCl (Merck) were used as purchased.

2.2. Instrumentation

The analytes were separated by using a chromatographic system comprised of a Shimadzu on-line degassing system DGU-14A coupled to a FCV-10AL controller unit and a LC-10AD high-pressure solvent delivery pump, with a 20 μL sample loop injector. Analytes identification and quantitation was performed with a SPD-M6A UV/diode-array detector working under the Class M10A Software (Version 1.20). The column material was an APEX C_{18} (Jones Chromatography, UK), with particle size of 5 μm (25 cm × 4.6 mm I.D.). Isocratic elution was used for the elution of the UV absorbing from the column with a mobile phase composed of acetonitrile/water (80%/20%, v/v). Column temperature was set at 30 °C and the data collection was performed by obtaining one spectrum per second. The peaks representing the target species were recognized both by the retention time and their spectrum pattern. Turbidity measurements were performed at 300 nm with a Jenway 6402 UV–vis spectrophotometer.

A thermostated bath maintained at the desired temperatures was used for the temperature experiments. The pH of the solutions was measured using a Radiometer Copenhagen digital pH-meter type PHM83 with 0.01 pH resolution over the pH range of 2–10.

2.3. Advesicle-solid-phase dispersion (ASPD)

In 250 mL of Hepes buffered (pH 8.2, $C > 10$ mM) aquatic solution (20 °C) containing the analytes in 0.2 M NaBr, appropriate volume of DDAB solution was added to yield a final concentration of 7×10^{-4} M. The mixture was sheared by vortexing for 2 min to aid the formation of vesicles and 50 mg of dry silica were added. The vials were stirred for 10 min (or twice vortexed for 5 min) to uniformly disperse the silica and enable the adhesion of the vesicles carrying the analytes on the negatively charged surface. The mixture was

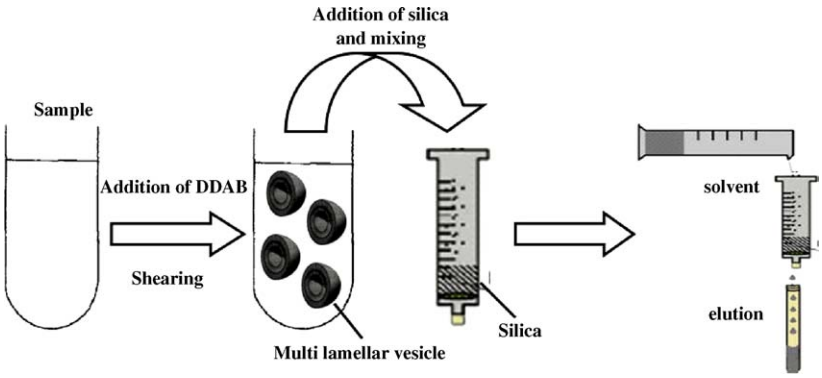

Fig. 1. Schematic representation of the ASPD extraction procedure.

then filtered to collect the sorbent. The elution step was carried out with 0.5 mL of methanol. The final extract was directly injected into the liquid chromatograph through a 20 μL loop. A schematic representation of the procedure is depicted in Fig. 1.

2.4. Advesicle-solid-phase extraction (ASPE)

Solid-phase extraction experiments were conducted with 50 mg of silica embedded into a 3 mL cartridge (J.T. Baker, USA). The silica was conditioned with doubly distilled water and a few milliliter of buffer solution to activate the silica surface. Then, 50 mL of aquatic solution was percolated under vacuum at a flow rate of 10 mL min^{-1}. Elution of the analytes was carried out with 500 μL of methanol.

3. Results and discussion

The actual form of any surfactant aggregate depends on the molecular constitution of the amphiphile. DDAB is roughly a cylinder-shape molecule favouring the formation of bilayers in water [14]. Depending on the experimental conditions, like surfactant concentration, temperature and the presence of electrolytes various structures can be formulated; for the purposes of this study only the dilute region (up to 2.5% or 5×10^{-2} M) will be considered.

Preliminary experiments with off-line SPE showed that analyte recoveries were rather mediocre. Literature reference to this problem revealed that vesicle adhesion onto oppositively charged surfaces requires strong stimulus a case which is not satisfied with SPE [15,16]. Thus, an alternate procedure was pursed. Solid-phase dispersion (SPD) was an intriguing alternative since it necessitates mixing of the sample with a proper solid matrix in order to enable the isolation of the analytes. Although SPD is not unusually applied to water samples, it offers the required flexibility and was decided for the subsequent work.

In order to obtain the optimum working conditions various parameters were assessed for their effect on the analytical performance based on a univariate experimental procedure. The overall examined and selected parameters are presented in Table 1 for quick reference.

3.1. Adsorption of vesicles on silica surface

The adsorption of DDAB vesicles in aquatic solutions was followed by turbidity measurements at 300 nm. The experimental isotherm of Fig. 2 belongs to the H type with a maximum which indicates the high affinity of the adsorbate for the surface probably due to the formation of ion pairs between the deprotonated silanol and the quaternary ammonium polar heads of the bilayer (proton/tetraalkylammonium exchange) [15]. According to this isotherm DDAB vesicles are completely adsorbed at low concentrations while for higher concentrations vesicle/vesicle interactions act as scavengers of vesicle excess at the silica surface reducing the adsorbed amount of DDAB [16]. The plot of Fig. 2 shows that the maximum amount of DDAB vesicles adsorbed was 5×10^{-4} M/mg silica (or 4.62 mg DDAB/mg silica) which is significantly higher than those reported for single and double chain cationic surfactants on various silica sorbents as well as on anionic admicelles formation on alumina from single or double chain anionic surfactants [3,6,17–19]. This behavior is attributed to three reasons; the high affinity of the vesicular aggregates for the silica surface, the properties of the selected sorbent and to the fact that vesicles adhere onto the surface intact without disrupting their structure [20]. According to the latter, the adsorbed vesicles should create a three-dimensional layer in the solid-liquid interface which significantly enhances contact with the components of the bulk solvent as opposed to the two-dimensional network observed in admicelles formation [20,21].

Table 1
Studied parameters and selected values for the proposed method

Parameter	Range tested	Selected value
DDAB (M)	5×10^{-5}–7×10^{-3}	7×10^{-4}
NaBr (M)	0.05–2.0	0.2
pH	2–10	8.0–8.5
Hepes buffer (mM)	5–40	10
Breakthrough Volume (mL)	100–1000	≤400
Shearing time (min)	1–20	2
Mixing time (min)	1–30	10
Elution solvent (methanol) (μL)	250–2000	≥500

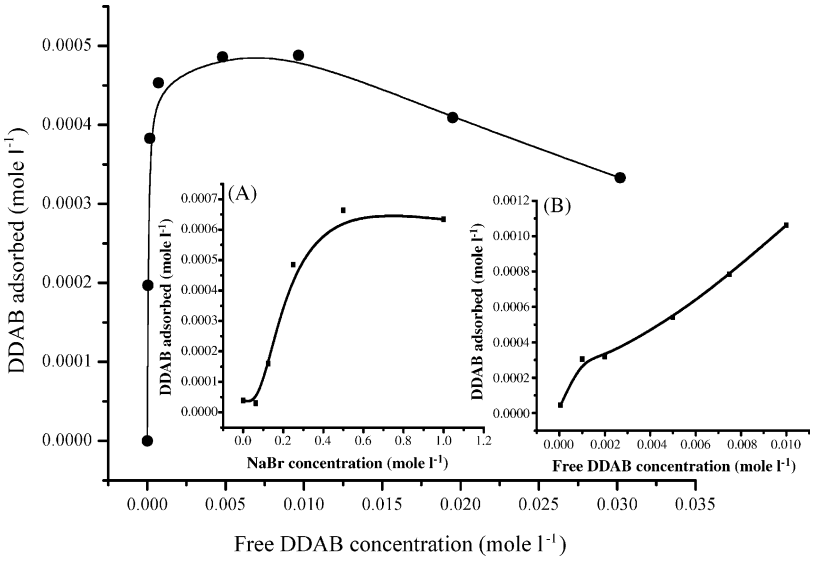

Fig. 2. Experimental adsorption isotherm of DDAB onto silica in Hepes buffered aquatic solution. [Hepes] = 10 mM (pH 8.2), silica 50 mg. Inset A: [DDAB] = 7×10^{-4} M; [NaBr] = 0.05–2.0 M. Inset B: [NaBr] = 0.1 M.

3.2. Effect of shearing on vesicle formation and adsolubilization

A central point in the application of vesicles is their preparation as in many cases input of external energy may be required [8]. DDAB is known to form vesicles upon simple dilution to water [13,22]. However, external stimulus may change the rate and properties of the formulated vesicular assemblies thus influence the extraction performance. To investigate the influence of external energy input on vesicle formation, the vials were sheared (vortexed or steared) for 1–30 min. Once the solutions have been sheared there was no variation in the extraction performance over the entire time period examined. Since in almost all circumstances it is necessary to apply some sort of shear to the system to homogenize it, the formation of vesicles is inherently ensured. To ensure equilibrium with regards to vesicle growth and formation 2 min of shearing was decided.

According to previous studies, to instigate vesicles adhesion onto the silica surface the input of external stimulus is imperative [15,16]. To study the influence of stimulus on the extraction performance end-over-end mixing, vortexing, stirring and sonication were examined. Sonication was inadequate possibly due to incomplete dispersion of the silica particles with the bulk aqueous solvent. End-over-end mixing produced satisfactory recoveries but caused intense foaming. Vortex mixing and stirring alleviated the problem of intense foaming and provided high recoveries only within a few minutes of shearing which is further advantageous since it does not increase the time of analysis. To enable complete vesicle deposition, the mixtures were stirred for 10 min.

3.3. Influence of DDAB concentration

In the absence of DDAB the examined UV filters hardly adsorbed onto the silica surface. For all compounds percentages of adsorption lower than 2% were obtained. However, on salt addition this situation changed especially for the more hydrophobic homologues. Thus, E6300 and E2292 were detected after extraction with simple salt addition. This was attributed to the change in the solvation environment of non-polar analytes which become less water-soluble in the presence of salts showing high affinity for the silica surface through hydrophobic interactions. The higher percentage recoveries were lying around 20% for E6300 and 30% for E2292. This again, necessitated the examination of blank effects in order to assess the influence of the studied parameters without co-estimating salt effect.

When DDAB was added to the solution the situation changed dramatically. Fig. 3 shows the adsolubilization of the target species on DDAB-coated silica at pH 8.2. It is evident that DDAB significantly enhanced the extraction performance especially of the more hydrophilic analytes. Interestingly, the more hydrophobic the analytes are the more amount of DDAB is required to enhance their extraction. This is ascribed to the relatively limited capacity of vesicles, compared to pure micellar clusters, to encapsulate hydrophobic complexes [23],

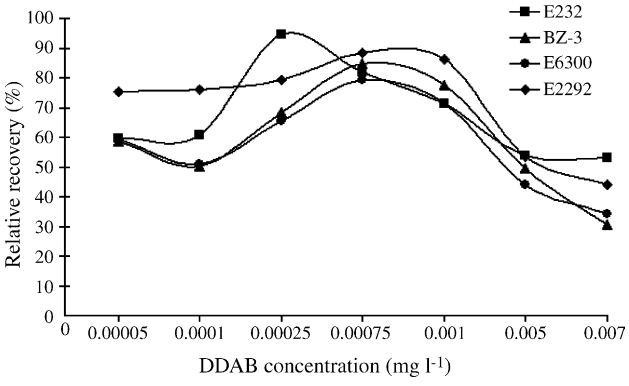

Fig. 3. Effect of DDAB concentration on the recovery of the analytes. [Hepes] = 10 mM (pH 8.2), [NaBr] = 0.1 M, silica 50 mg.

due to their charged nature and strong packing of surfactant molecules, resulting in highly density hydrocarbon cores, which lessens solubilization [19,23,24]. Greater DDAB amounts gradually decreased the adsolubilization due to competition of vesicles in solution that alters the structure of the adsorbed bilayers and reduces the adsorbed amount, as previously discussed. An amount of 7×10^{-4} M was finally decided to compromise between hydrophilic–hydrophobic solubilization sites.

3.4. Influence of sorbent amount and treatment

Since the overall process is controlled by the adsolubilization of DDAB vesicles on silica surface the efficacy of the method would be directly related to the charge density of the mineral oxide thus on the amount of silica. Although the amount of sorbent is rarely a limitation in batch procedures we decided to study the influence of silica amount since no previous study was available on this topic. Our data indicate that an amount of 50–100 mg is the optimum especially for the more hydrophobic analytes. For higher amounts a slight reduction is observed (<5%) possibly due to single bilayer deposition.

Preparation of silica surface prior to advesicle deposition was the next parameter examined for its effect of the analytical performance. Pre-treatment of silica with acid resulted in higher turbidity of the bulk aqueous phase after each extraction in unbuffered solutions indicating the decrease in surfactant adsorption. This is rationalized by the fact that acid treatment reduces the charged surface sites thus providing fewer nucleation sites for surfactant adsorption [25]. However, in our experiments, acid treatment did not affect analyte extraction due to regulation of the solution pH and ionic strength. Nonetheless, pH was slightly reduced, which can be easily regulated by using a more concentrated buffer as will be discussed further below.

3.5. pH and buffer effects

The charge of silica surface strongly depends on the pH of the solution thus, the maintenance of the appropriate pH value is essential to the overall process. Varying the solution pH from 2 to 10 enabled us to identify some intriguing mechanisms involved in the proposed extraction pattern. Evidently, acidic pH values enabled the extraction of more hydrophobic analytes declining as analyte hydrophilicity increased. This is attributed to the uncharged nature of silica at low pH which enhances hydrophobic interactions with the target species (especially in the presence of inorganic salts). As pH increased, extraction performance was reduced starting to increase again at pH values above 7. This behaviour is consistent with the surface charge density of silica starting from −1 at pH 6 and increasing up to −18 at pH of 8.2 which promotes DDAB vesicles adsorption [25]. According to our results, pH values above 8 should be maintained to ensure maximum vesicles adhesion on the negatively charged silica. Although higher pH values gave somehow better results they were not applied due to the unavailability of appropriate buffer media with effective pH range in such alkaline conditions. It is worth mentioning that sunscreen agents behave like weak acids thus in the alkaline media they are present as their ionized forms. The increased extraction with increasing pH suggests that analyte partitioning is not only governed by hydrophobic interactions but also by interactions with the hydrophilic vesicular core or even with the charged surface of the vesicle aggregates.

However, previous studies have shown that silica surface charge varies not only with pH, but also with surfactant adsorption owing to the ionization of surface groups [25]. Hence, the maintenance of the optimum pH value is essential to the overall process. To control the pH of the solution the application of a buffer medium was decided over pH adjustment. Inorganic buffers were not examined at all, since their anionic counterions can react with the cationic vesicles and alter the observed behaviour. Although a variety of organic buffers with effective pH range in the desired values are commercially available, only Tris and Hepes have been investigated with regards to their effect on vesicles adsorption. According to these studies, Hepes causes a systematically larger surfactant adsorption compared to Tris and for this reason it was selected for the subsequent work [15,16]. Varying Hepes concentration in the range of 5–40 mM was not found to influence either sample pH or analyte recoveries. Thus, a concentration of 10 mM was applied throughout.

3.6. Effect of inorganic electrolytes

The addition of inorganic electrolytes, not only influences the extraction efficiency by altering the solvation environment of the target analytes but also induces significant changes in vesicle structure and growth and consequently on their adherence onto the silica surface [25] which is the main mechanism of analyte isolation from the bulk aqueous phase.

Extraction performances in the presence of increasing amounts of various inorganic electrolytes were investigated. Four inorganic salts, $NaNO_3$, NaBr, NaCl and KCl were selected based on their counterions and co-ions since it is well recognised that inorganic counter-ions affect the structure of vesicles while co-ions influence their adsorption behaviour [25–27]. Blank solutions (without DDAB) were also analysed to assess the net salt effect (direct adsorption on silica). Our data indicate that the net salt effect was decreasing according to the order $NaNO_3$ > KCl > NaCl > NaBr for E6300 and E2292 while smaller effects were attained for the other analytes (especially at high salt content) which suggests that ionic strength had a more pronounced effect on hydrophobic rather than in hydrophilic species. For all salts investigated, analyte extraction was amended with increasing salt content reaching a plateau and dropping again as concentration increases (Fig. 4). This was attributed to the increase of DDAB vesicles deposition on the solid sorbent. The results obtained with NaBr (inset graphs of Fig. 2) reveal a two-fold increase in vesicles deposition (9.83 mg DDAB/mg silica) a situation which amends the partition of the analytes without risking saturation of the solubilization sites. For higher electrolyte concentrations hypertonic stress causes vesicle breakdown [28] and consequently their release from the silica surface reducing the extraction performance.

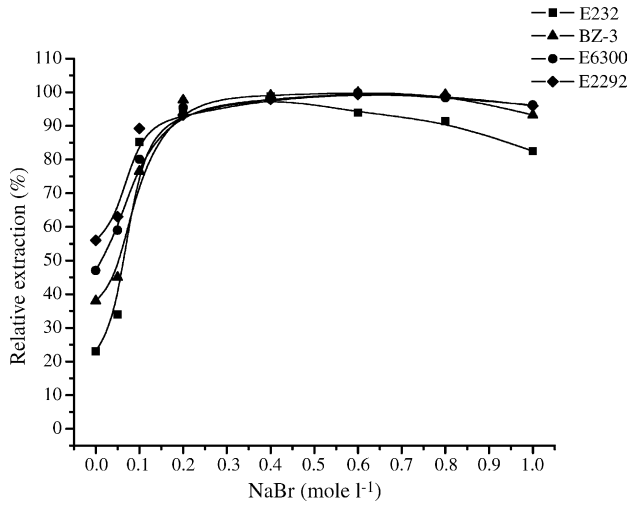

Fig. 4. Effect of inorganic electrolyte (NaBr) on analytes recovery. [DDAB] = 7×10^{-4} M. [Hepes] = 10 mM (pH 8.2), silica 50 mg.

3.7. Effect of temperature

The effect of temperature was also studied since it is known to affect the vesicle formation/breakdown interactions. Our data indicate (not shown for brevity) that low temperatures aid the extraction of the target analytes which is in agreement with the phase transition temperature of DDAB (about 12 °C) [29]. As temperature increases, turbidity gradually declines indicating the acceleration of vesicles dissolution through a transition from a lamellar phase to a lamellar dispersion and finally to vesicle breakdown [13]. In concurrence with our previous observations on anionic vesicles [30], low temperatures (up to 25 °C) pose as no threat to the formation and stability of the vesicular aggregates.

3.8. Effect of single-chain surfactants

Significant changes in the phase behaviour of DDAB–water systems are brought about following the addition of single-chain surfactants as a result of the electrostatic interactions within and among the aggregates [13]. In our system, the addition of single-chain surfactants did not affect the analytical performance for concentrations up to 0.2 mM but deteriorated the extraction of all analytes at concentrations above 0.25 mM primarily due to vesicle breakdown and secondarily due to competition for silica adsorption sites. Since no improvement was attained, the addition of a single-chain surfactant was not further considered.

3.9. Desoprtion solution

The ability of various solvents to disrupt advesicles and extract the analytes from the silica surface was investigated. Methanol, acetonitrile, water, NaCl (0.1 M), HCl (0.2 M) and NaOH (0.2 M) were tested for that purpose. Water, sodium chloride, hydrochloric acid and sodium hydroxide produced low recoveries so they were not further considered. Organic solvents like methanol and acetonitrile efficiently eluted the adsorbed analytes, owing to their ability to disrupt vesicles. To pursue maximum preconcentration 500 μL of methanol were finally selected.

Table 2
Extraction recovery (%) ± standard deviation of 50 nM of the target compounds with solid-phase dispersion (SPD) and solid-phase extraction (SPE) under the optimum experimental conditions

	% recovery ± standard deviation	
	SPD	SPE
E232	98.2 ± 1.2	76.1 ± 5.0
Bz-3	97.4 ± 1.6	65.2 ± 5.8
E6300	98.8 ± 2.0	64.9 ± 5.9
E2292	99.6 ± 2.1	67.2 ± 6.3

3.10. Advesicle solid-phase dispersion versus advesicle solid-phase extraction

The possibility of applying off-line solid-phase extraction was re-assessed under the optimum experimental conditions established above. The results of Table 2 show that off-line solid-phase extraction produced low recoveries while solid-phase dispersion gave significantly better results. In the ASPD mode the vesicles are allowed to equilibrate with silica surface through intense mixing thus ensure complete deposition. On the contrary, during ASPE vesicle aggregates bearing the target species are only partially retained by the sorbent without reaching equilibrium due to antagonism between vesicles. As the procedure continues, clogging of the cartridge is observed, as a function of DDAB concentration, possibly due to saturation of the silica reactive sites a situation which deteriorates the extraction performance and reduces the preconcentration factors.

3.11. Breakthrough volume

The breakthrough volume of the ASPD procedure was estimated by preconcentrating samples of increasing volumes (100–1000 mL) containing the same amount of analytes. Breakthrough was considered to occur when the amount eluted decreased about 5%. Measurement of the peak areas eluted from the sorbent revealed that sample volumes up to 400 mL could be used under the proposed experimental conditions. For higher sample volumes the extraction performance was irreproducible possibly due to the uncertainty encountered during the handling of large sample volumes.

3.12. Sorbent regeneration

Because of the high capacity of advesicles to solubilize matrix components, the regeneration of the sorbent material necessitates the complete removal of any adsorbed sample constituents as well as the surfactant bilayer aggregates. To ensure complete removal of any adsorbed or adsolubilized compounds methanol was re-applied and completely removed with water. The silica surface was then conditioned with 0.005 M NaCl to restore Na^+ content of the surface and washed with water to remove any

Table 3
Analytical features of the method

Parameter	E232	Bz-3	E6300	E2292
Preconcentration factor	500	500	500	500
Extraction-concentration factor	0.97	0.98	1.01	1.03
LOD ($\mu g\,L^{-1}$)[a]	0.18	1.10	0.64	0.47
RSD (%), $n=5$	3.54	3.88	4.15	4.58
Calibration graphs	$S^b = 1.4 \times 10^5\ (\pm 2.0 \times 10^3) + 3.3 \times 10^7\ (\pm 3.3 \times 10^5) \times C$	$S^b = -2.7 \times 10^4\ (\pm 4.5 \times 10^3) + 1.2 \times 10^7\ (\pm 1.2 \times 10^5) \times C$	$S^b = -2.1 \times 10^4\ (\pm 6.7 \times 10^3) + 3.1 \times 10^7\ (\pm 3.0 \times 10^5) \times C$	$S^b = -4.2 \times 10^3\ (\pm 3.1 \times 10^3) + 2.0 \times 10^7\ (\pm 1.4 \times 10^5) \times C$
Correlation coefficient (r^2)	0.9994	0.9993	0.9995	0.9997

[a] Limit of detection defined as three times the signal to noise ratio.
[b] S = peak area (arbitrary units); C = mg L^{-1}.

excess ions. The regenerated dry sorbent worked for at least 10 extractions without deterioration.

4. Analytical merits

Calibration curves were obtained by preconcentrating 250 mL of standard solutions under the defined experimental conditions. Linear relationships between the produced signals and the concentrations were found for all compounds investigated. The parameters of the individual calibration curves together with the calculated detection limits (three times the signal to noise ratio) and the relative standard deviation for five samples are gathered in Table 3. Our data suggest that 0.8 mg of analytes are retained on each mg of silica modified with 10 mg of DDAB which is higher than those obtained with cationic or anionic admicelles of either single or double chain surfactants [3,6,17,18]. Preconcentration factors of 500 were achieved with extraction concentration factors close to unity, suggesting quantitative recovery of the analytes. Higher preconcentration factors and consequently lower detection limits can be achieved by either evaporating the methanolic extract to lower volume or by increasing sample volume up to 400 mL or even both.

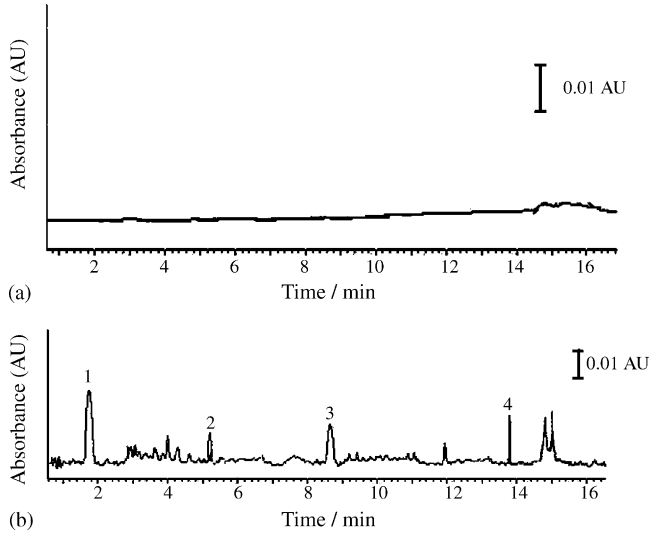

Fig. 5. Chromatograms of Swimming pool water to which 10 nM of sunscreen agents were added: (a) without preconcentration; (b) with advescile solid-phase dispersion. Chromatographic conditions as mentioned in the text.

5. Application to water samples

The application of the present method to the preconcentration of the target analytes from 250 mL water sample for HPLC analysis is presented in Fig. 5. Direct injection to the HPLC system of swimming pool water spiked with 10 nM of E232, Bz-3, E6300 and E2292 produced no peaks in the chromatogram (Fig. 5(a)). In contrast, all compounds were apparently observed after 500-fold preconcentration (Fig. 5(b)), which indicates the suitability of the method for determining these compounds at trace levels.

The detection of the target compounds in distilled water served to calculate the recoveries over a concentration range from 10 to 100 nM. The data indicate recoveries in the range of 96–103% which is close to those reported in previous studies dealing with the determination of personal care products in bathing waters [31,32].

6. Conclusions

The analytical utility of vesicular aggregates supported on mineral oxides (advesicles) as sorbents for the extraction of organic compounds from aqueous matrices has been demonstrated. Based on the results obtained, the present approach provides a new insight into the analytical applications of organized surfactant assemblies by extending the scope and application of previous analytical procedures based on adsolubilization. That is because this novel method alleviates the need to manipulate inorganic salt concentration since the addition of salts enhances the extraction performance and ensures method reproducibility. Moreover, there is no need to pre-treat the sorbent (silica oxide) since vesicle deposition is a rapid process accomplished by simple mixing of the sorbent with the vesicular solution.

Considering the rich structural variety of vesicles and the availability of mineral surfaces (also including zeolites), one can visualize the vastness of alternative options that can be deployed by designing specifically oriented analytical methods towards the conveyance from selective to non-selective extractions of organic molecules or vice versa. The on-line set-up coupling of advesicle-based solid-phase extraction to liquid chromatography is probably the most challenging step forward and further research is oriented towards this direction.

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